CONCENTRATION OF BIOPETROL SYNTHESIZED FROM OLEIC ACID THROUGH CATALYTIC CRACKING USING ZEOLITE AS CATALYST

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DECLARATION

I declare that this thesis entitled *"Concentration of Biopetrol Synthesized from Oleic Acid through Catalytic Cracking using Zeolite as Catalyst"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....

Name : Nurul Liana bte Abd Rahman

Date : APRIL 2009

DEDICATION

Specially for;

My beloved parent, Abd Rahman bin Jantan and Zainon bte Abdullah,

Also my siblings, with memory of my late grandmother,

Who always stand by my side whenever I need them…

Thankful to:

My supervisor for his kindness helping me all the way

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ABSTRACT

Oleic acid is one of the major fatty acid in vegetable oil. In this research, zeolite catalysts are used over the conversion of oleic acid into isooctane as the future biopetrol in a heating mantle at atmospheric pressure. The main purposed of studies is to improve the concentration of isooctane using catalytic cracking method. The effect of various amount of Zeolite catalyst at 1g, 5g, 10g and 20g and various dilution factor of isooctane to hexane at 1%, 5%, 10% and 20% are studied over the yield of biopetrol at 98^{o}C. Gas chromatography is used for the qualitative and quantitative analysis of the samples. Backward calculation is applied to calculate the actual concentration of isooctane in the distilled oleic acid. The maximum yield of desired isooctane obtained at 20g of catalyst and dilution of 20% isooctane to hexane is recorded at 7.89%. Experimental works has successful show that catalytic cracking is greater in conversion than thermal cracking.

ABSTRAK

Asid Oleik adalah salah satu asid lemak utama di dalam minyak sayuran. Dalam kajian ini, agen pemangkin Zeolite telah digunakan untuk memperolehi isooktana daripada asid oleik untuk dijadikan sebagai biopetrol pada masa akan datang dengan menggunakan pemanas mantel pada tekanan atmosphera. Tujuan utama kajian ini dijalankan adalah untuk memperbaiki kepekatan isooktana menggunakan kaedah penguraian agen pemangkin. Kesan perubahan jumlah agen pemangkin Zeolite pada 1g, 5g, 10g dan 20g serta perubahan faktor pencairan isooktana kepada heksana pada 1%, 5%, 10% dan 20% dikaji terhadap penghasilan biopetrol pada suhu 98^{o}C. Alat Gas Kromatografi telah digunakan untuk kualitatif dan kuatitatif analisis semua sampel. Pengiraan semula kepekatan isooktana tanpa pencairan heksana digunakan untuk mengira kepekatan sebenar isooktana di dalam didihan asid oleik. Kepekatan maksimum isooktana dicatatkan pada 20g agen pemangkin dan pada 20% cairan isooktana kepada heksana iaitu sebanyak 7.89%. Experimen ini telah berjaya membuktikan penguraian menggunakan kaedah agen pemangkin lebih bagus berbanding kaedah penguraian haba.

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LIST OF SYMBOLS

P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
^{o}C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
m	-	Meter
n	-	Number of moles
L	-	Liter

LIST OF APPENDICES

LIST OF SAFETY PHRASE CODES

S1	Keep locked up
S(1/2)	Keep locked up and out of the reach of children
S2	Keep out of the reach of children
S3	Keep in a cool place
S3/7	Keep container tightly closed in a cool place
S3/7/9	Keep container tightly closed in a cool, well-ventilated place
S3/9/14	Keep in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer)
S3/9/14/49	Keep only in the original container in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer)
S3/9/49	Keep only in the original container in a cool, well-ventilated place
S3/14	Keep in a cool place away from ... (incompatible materials to be indicated by the manufacturer)
S4	Keep away from living quarters
S5	Keep contents under ... (appropriate liquid to be specified by the manufacturer)
S6	Keep under ... (inert gas to be specified by the manufacturer)
S7	Keep container tightly closed
S7/8	Keep container tightly closed and dry
S7/9	Keep container tightly closed and in a well-ventilated place
S7/47	Keep container tightly closed and at temperature not exceeding ... ^{O}C (to be specified by the manufacturer)
S8	Keep container dry
S9	Keep container in a well-ventilated place
S12	Do not keep the container sealed
S13	Keep away from food, drink and animal feedingstuffs
S14	Keep away from ... (incompatible materials to be indicated by the manufacturer)
S15	Keep away from heat
S16	Keep away from sources of ignition - No smoking
S17	Keep away from combustible material
S18	Handle and open container with care
S20	When using do not eat or drink
S20/21	When using do not eat, drink or smoke
S21	When using do not smoke

S22	Do not breathe dust
S23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
S24	Avoid contact with skin
S24/25	Avoid contact with skin and eyes
S25	Avoid contact with eyes
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S27	Take off immediately all contaminated clothing
S27/28	After contact with skin, take off immediately all contaminated clothing, and wash immediately with plenty of ... (to be specified by the manufacturer)
S28	After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer)
S29	Do not empty into drains
S29/35	Do not empty into drains; dispose of this material and its container in a safe way
S29/56	Do not empty into drains, dispose of this material and its container at hazardous or special waste collection point
S30	Never add water to this product
S33	Take precautionary measures against static discharges
S35	This material and its container must be disposed of in a safe way
S36	Wear suitable protective clothing
S36/37	Wear suitable protective clothing and gloves
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection
S36/39	Wear suitable protective clothing and eye/face protection
S37	Wear suitable gloves
S37/39	Wear suitable gloves and eye/face protection
S38	In case of insufficient ventilation wear suitable respiratory equipment
S39	Wear eye/face protection
S40	To clean the floor and all objects contaminated by this material use ... (to be specified by the manufacturer)
S41	In case of fire and/or explosion do not breathe fumes
S42	During fumigation/spraying wear suitable respiratory equipment (appropriate wording to be specified by the manufacturer)
S43	In case of fire use ... (indicate in the space the precise type of fire-fighting equipment. If water increases the risk add - Never use water)
S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
S46	If swallowed, seek medical advice immediately and show this container or label
S47	Keep at temperature not exceeding ... ^{O}C (to be specified by the manufacturer)
S47/49	Keep only in the original container at temperature not exceeding ... ^{O}C (to be specified by the manufacturer)
S48	Keep wet with ... (appropriate material to be specified by the manufacturer)
S49	Keep only in the original container
S50	Do not mix with ... (to be specified by the manufacturer)
S51	Use only in well-ventilated areas

S52	Not recommended for interior use on large surface areas
S53	Avoid exposure - obtain special instructions before use
S56	Dispose of this material and its container at hazardous or special waste collection point
S57	Use appropriate containment to avoid environmental contamination
S59	Refer to manufacturer/supplier for information on recovery/recycling
S60	This material and its container must be disposed of as hazardous waste
S61	Avoid release to the environment. Refer to special instructions/safety data sheet
S62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label
S63	In case of accident by inhalation: remove casualty to fresh air and keep at rest
S64	If swallowed, rinse mouth with water (only if the person is conscious)

LIST OF RISK PHARASES

Risk phrases, coded in the form R34, R61 etc are now included in MSDS sheets for chemicals purchased in the UK and in many other countries. A list of the meaning of these codes area available as below:

- R1 Explosive when dry.
- R2 Risk of explosion by shock, friction, fire or other source of ignition.
- R3 Extreme risk of explosion by shock, friction, fire or other sources of ignition.
- R4 Forms very sensitive explosive metallic compounds.
- R5 Heating may cause an explosion.
- R6 Explosive with or without contact with air.
- R7 May cause fire.
- R8 Contact with combustible material may cause fire.
- R9 Explosive when mixed with combustible material.
- R10 Flammable.
- R11 Highly flammable.
- R12 Extremely flammable.
- R13 Extremely flammable liquefied gas
- R14 Reacts violently with water.
- R15 Contact with water liberates extremely flammable gases.
- R16 Explosive when mixed with oxidizing substances.
- R17 Spontaneously flammable in air.
- R18 In use may form inflammable/explosive vapor-air mixture.
- R19 May form explosive peroxides.
- R20 Harmful by inhalation.
- R21 Harmful in contact with skin.
- R22 Harmful if swallowed.
- R23 Toxic by inhalation.
- R24 Toxic in contact with skin.
- R25 Toxic if swallowed.
- R26 Very toxic by inhalation.

- R27 Very toxic in contact with skin.
- R28 Very toxic if swallowed.
- R29 Contact with water liberates toxic gas.
- R30 can become highly flammable in use.
- R31 Contact with acids liberates toxic gas.
- R32 Contact with acid liberates very toxic gas.
- R33 Danger of cumulative effects.
- R34 Causes burns.
- R35 Causes severe burns.
- R36 Irritating to eyes.
- R37 Irritating to respiratory system.
- R38 Irritating to skin.
- R39 Danger of very serious irreversible effects.
- R40 Limited evidence of a carcinogenic effect.
- R41 Risk of serious damage to the eyes.
- R42 May cause sensitization by inhalation.
- R43 May cause sensitization by skin contact.
- R44 Risk of explosion if heated under confinement.
- R45 May cause cancer.
- R46 May cause heritable genetic damage.
- R47 May cause birth defects
- R48 Danger of serious damage to health by prolonged exposure.
- R49 May cause cancer by inhalation.
- R50 Very toxic to aquatic organisms.
- R51 Toxic to aquatic organisms.
- R52 Harmful to aquatic organisms.
- R53 May cause long-term adverse effects in the aquatic environment.
- R54 Toxic to flora.
- R55 Toxic to fauna.
- R56 Toxic to soil organisms.
- R57 Toxic to bees.
- R58 May cause long-term adverse effects in the environment.
- R59 Dangerous to the ozone layer.
- R60 May impair fertility.
- R61 May cause harm to the unborn child.
- R62 Risk of impaired fertility.
- R63 Possible risk of harm to the unborn child.
- R64 May cause harm to breastfed babies.
- R65 Harmful: may cause lung damage if swallowed.
- R66 Repeated exposure may cause skin dryness or cracking.
- R67 Vapours may cause drowsiness and dizziness.
- R68 Possible risk of irreversible effects.

LIST OF UN HAZARD CLASSIFICATION SYSTEM

1. Class 1 Explosive
    a. 1.1 Substances with a mass explosion hazard
    b. 1.2 Substances which present a projection hazard but no mass explosion hazard
    c. 1.3 Substances which present both a fire hazard and a minor blast or projection hazard (or both) but not a mass explosion hazard
    d. 1.4 No significant hazard
    e. 1.5 Very insensitive substances with a mass explosion hazard
    f. 1.6 Very insensitive articles with no mass explosion hazard
2. Class 2 Gases
    a. 2.1 Flammable gases
    b. 2.2 Non-flammable, non-toxic gases
    c. 2.3 Toxic gases
3. Class 3 Flammable liquids
4. Class 4 Flammable solids
    a. 4.1 Flammable solids, self-reactive substances and solid desensitized explosives
    b. 4.2 Materials liable to spontaneous combustion
    c. 4.3 Substances which, in contact with water, release flammable gases
5. Class 5. Oxidizing substances and organic peroxides
    a. 5.1 Oxidizing agents
    b. 5.2 Organic peroxides
6. Class 6 Toxic and infectious substances
    a. 6.1 Toxic substances
    b. 6.2 Infectious substances
7. Class 7 Radioactive substances and articles
8. Class 8 Corrosive substances
9. Class 9 Miscellaneous dangerous substances

CHAPTER 1

INTRODUCTION

1.0 Introduction

Biofuels for transport, including bioethanol, biodiesel, biogas and biopetrol have enormous potential to displace a depletion amount of conventional fossil-derived fuels around the world over the next decades. Biofuel sources particularly vegetable oil have recently grabbed many researchers attention via their wide availability and renewably. Instead of environmental friendly, several evidences showed that the usage of biofuel also can improve the engine efficiency. Biodiesel for example performed excellent energy balance (input; 1/ output; 2.5) which would be 78 % greater than standard diesel. (Herschel, 2007) Generally, biofuel is defined as a liquid or gaseous fuel that can be produced from the utilization of biomass substrates according to Giampietro *et al.* (Tamunaidu and Bhatia, 2006) In this research production of biopetrol is the main topic that being focused.

Commonly, natural triglycerides present in vegetable oil are extracted into several oil components using transterification route but it generates a large amount of glycerin (byproduct) thus difficult to purify. Therefore, catalytic cracking method is suggested. However, triglyceride molecules are too large to enter the pores of Zeolite (Dupain *et al*, 2006) during catalytic cracking; therefore this research is proceeding within vegetable oil derived or fatty acid into biopetrol at 1 atm and at

98^{o}C. In this case, oleic acid ($C_{18}H_{34}O_2$) has been chosen for conversion into isooctane which also the major constituents of biopetrol since that oleic acid contain low in sulfur and nitrogen besides it also encounter more than 40% constituents inside most of the vegetable oil such as palm oil, olive oil, rapeseed and others. Beside, Zeolite also is chosen because it possesses a catalytic activity that is much higher than other types of catalysts because of its high selectivity properties.

Twaiq *et al* in his paper claimed that, recently several researchers have been successful in production of hydrocarbons from palm oil mainly bio-gasoline or biopetrol (Tamunaidu and Bhatia, 2006) which have been carried out using cracking catalysts in a micro-reactor but still not valid for commercialize. It also has generated a significant of interest of Palm Oil Research Institute of Malaysia (PORIM) in development of biodiesel from palm oil. (Hussain *et al*, 2006)

1.1 Research Background and Problem Statement

With concern to the global warming growing unstable, reduction of energy supplier and the increasing of global crude oil prices that up to RM 2.70 per liter for petrol while RM 2.58 per liter for diesel in Malaysia started 1st July 2008 and not counting other world countries that suffer oil barrenness because of their geography area, it believes that biopetrol will fulfill the worldwide demand for, in the future. Compared with ethanol and biodiesel as currently cleaner-burning alternatives, biopetrol is still newcomer. But if the governments take seriously pushing it to the recent market within development technology activity it will not be surprising that biopetrol will take over the renewable energy market.

As noted earlier, one factor that leads to increasing of oil prices is that our oil reserves can not stand much longer and we are unable to be the net exporter of